High-accuracy calculations for heavy and superheavy elements

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Accurate calculations for very heavy elements require high-order inclusion of both relativity and electron correlation. The framework of our method is the Dirac-Coulomb-Breit Hamiltonian, which includes relativistic terms up to second order in α, the fine-structure constant. This model is adequate for all atoms, as long as they are not highly ionized. The one-electron four-component Dirac-Fock-Breit spinors are obtained first, playing the same role as the Hartree-Fock orbitals in nonrelativistic quantum mechanics. Correlation is included via the coupled cluster method, which may be interpreted as infinite-order summation of large classes of perturbation terms, and has emerged as the most accurate approach for this purpose.

We are usually interested in studying a large number of states of a given atom. Since most of these states cannot be described, even approximately, by a single determinant, multireference coupled cluster methods are required. The essence of multireference methods is the partitioning of the function space into a small *P*, which comprises all the important determinants, and a large *Q*, the rest of the function space. The effect of *Q* is included by the CC scheme in an effective Hamiltonian constructed in *P*. This H_{eff} is then diagonalized, yielding the energies of all desired states simultaneously. Since the effect of *Q* is included approximately, whereas *P* is solved exactly by diagonalization, extending *P* will improve results. However, convergence of the CC iterations puts severe limitations on the structure and size of *P*. A new approach, the intermediate Hamiltonian coupled cluster, has recently been developed, allowing larger model spaces and greater flexibility in their construction, thereby extending the scope of the method and increasing its accuracy.

The method has been applied to many atoms, calculating energies of numerous states for each. Agreement with available experimental values was usually within a few hundredths of an eV. This makes the method a useful tool for reliable prediction of energy levels of superheavy elements.

Applications to transactinides include, *inter alia*:

- The ground state of Rf (E104) has been determined to be $7s^26d^2$, in contrast with previous predictions of $7s^27p^6d$. Correlation, which favors the d^2 configuration over dp, wins over relativity, which prefers the former configuration, leading to structure similar to that of Hf.
- E111 (eka-gold) is predicted to have a $6d^97s^2$ ground state, vs. the $(n-1)d^{10}ns$ structure of lighter coinage metals.
- The dication of E112 (eka-mercury), unlike Hg2+, shows very strong mixing of the d^8s^2, d^9s, and d^{10} levels in its low electronic states. The E112+ cation has the same electronic ground state as E111.
- E113 (eka-thallium) has a large (0.6eV) electron affinity, raising the possibility of $E113^-$ compounds. The d^9s^2 level of the dication is a mere 0.1 eV above the $d^{10}s$ ground state; this energy difference in Tl is over 8 eV. Di- and trivalent compounds of E113 with an open 6d shell could therefore exist.

- The ionization potential of E114 is 1.1 eV above that of Pb; in fact, it is higher than the IPs of all group-4 elements except carbon. This indicates that E114 will be less metallic and more inert than Pb.
- E118, a rare gas, is predicted to have positive electron affinity of 0.064(2) eV. QED effects on this value were calculated and found to decrease the EA by 9% or 0.0059(5) eV.
- The EA of E119 (eka-francium) is predicted to be 662 meV, much higher than for Cs (491 meV) or any other alkali atom.
- The ground state of E121 (eka-actinium) is $8s^2 8p$, vs. $ns^2(n-1)d$ of other group-3 elements.
- E122 (eka-thorium) will have an $8s^2 7d^8 p$ ground state, vs. the $7s^2 6d^2$ of Th.

These and other examples will be described.